



**PROCESS FOR REGENERATING AN AQUEOUS SOLUTION
CONTAINING METAL IONS AND SULFURIC ACID,
AS WELL AS AN APPARATUS**

The invention relates to a process for regenerating an aqueous solution containing metal ions and sulfuric acid, especially a solution containing zinc ions, nickel ions, iron ions and/or copper ions, in an electrolytic cell, wherein the metal ions are precipitated on the surface of the cathode and oxygen and protons are formed at the anode by hydrolysis, and regenerated solution can be returned to a preceding etching process or extraction process, as well as to an apparatus.

A disclosure is made in the textbook, "Praktische Galvanotechnik," published by Leuze Verlag of Saulgau/Wurttemberg, 1970, pages 537-538, of precipitating zinc out of sulfate electrolytes. Such sulfate electrolytes form in the conversion of zinc chloride solutions into zinc sulfate solutions by ion exchange methods, in which this preliminary step is intended to avoid any electrolytic treatment of chloride electrolytes because chlorine would be formed in the electrolytic treatment of zinc chloride electrolytes and would entail a considerable hazard.

Such a direct regeneration of a zinc chloride solution is disclosed in DE-OS 25 39 137, according to which the solution containing chloride ions is introduced into a cathode chamber in an electrolysis cell which is divided into three chambers, namely an anode chamber and a cathode chamber, with an electrolyte chamber arranged between them; the anode chamber is defined by a porous membrane of low permeability which separates the anolyte from the electrolyte, the anolyte containing sulfuric acid. The anolyte contains a substance which is capable of binding to the chloride ions that enter the anode

chamber and thus prevent oxidation of chloride ions at the anode. The liquid level of the anolyte is always maintained, by adding anolyte if necessary, so that the level is above the liquid level of the adjacent electrolyte for the purpose of sustaining the desired rate of flow through the membrane to achieve the technical purpose. In order to prevent any chloride ions that might seep through the anode membrane from being oxidized to chlorine gas, the anolyte contains a silver sulfate additive so as to assure the precipitation of the chloride as silver chloride.

The relatively complicated division of the electrolyte chamber into 3 chambers has been found problematical, as well as the use of membranes whose permeability can vary greatly in the course of the electrolytic process. Other problems can be seen in the addition of the silver sulfate chemical, in the formation of silver chloride and its removal from the cell, and in the danger of membrane clogging by silver chloride precipitates.

Furthermore, in the book, "Angewandte Elektrochemie," by A. Schmidt, Verlag Chemie Weinheim 1976, on page 210, requirements are given according to which zinc, in spite of its electronegative standard potential of $-0.763V$, can be precipitated owing to the high overvoltage of the hydrogen on the zinc; it is stated that for the precipitation of zinc a relatively high zinc ion concentration is necessary at the cathode, since otherwise, due to the increasing sulfuric acid concentration, after a certain time hydrogen would separate instead of zinc. On page 213 of the same book various examples of zinc electrolysis methods are given.

In EP-OS 0 435 382 there is disclosed an electrolysis process for treating old etchants containing metal ions; the cathode and anode chambers are



58 separated from one another by an anion exchanger membrane, the anode
59 chamber is filled with a demetallized oxidizable or nonoxidizable etching
60 solution and the freely chosen potential of the cathode or anode is kept
61 constant by means of a voltage-regulated rectifier through a reference
62 electrode; the metal ions are precipitated at the cathode and the regenerated
63 acid concentrated in the anode chamber is returned to the etching bath.

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65 However, no information can be found in EP-OS 0 435 382 on the treatment of
66 a solution containing metal ions with a sulfuric acid concentration that ranges
67 in practice, for example, from 60 to 80 grams per liter for an etching solution
68 in need of regeneration.

69
70 It is the purpose of the invention to describe a process by which sulfuric acid
71 etching or extracting solutions heavily loaded with metal ions can be
72 thoroughly demetallized, at the same time yielding a pure, highly concentrated
73 sulfuric acid. At the same time the cathodic separation of hydrogen, such as
74 can occur especially in aqueous solutions with a relatively low metal ion
75 concentration, is to be reliably prevented.

76
77 The process is to be used as an intermediate step in a chlorine gas-free
78 regeneration of etching or extracting solutions.

79
80 Furthermore, an apparatus is to be described for the regeneration of an
81 aqueous solution containing metal ions and sulfuric acid in an electrolysis cell
82 having at least one anode and one cathode, in which the electrolysis cell is
83 divided by an ion exchanger membrane into an anolyte chamber and a
84 catholyte chamber, the catholyte chamber has at least one opening for the
85 entry and exit of the solution containing metal ions, and the anolyte chamber



86 has at least one opening for the entry and exit of the regenerated solution.

87
88 The purpose is accomplished as regards the process by the fact that the
89 solution containing the metal ions is fed as anolyte with a sulfuric acid
90 concentration ranging from 60 to 80 g/l into an electrolysis cell divided by a
91 cation exchanger membrane stable against sulfuric acid, and that the cathodic
92 precipitation is performed at a current density ranging from 50 to 2500 A/m²;
93 cations migrate as metal ions and hydrogen ions from the anolyte through the
94 cation exchanger membrane into the catholyte on account of the voltage
95 present at the electrodes and are discharged, while the sulfuric acid
96 concentration in the anolyte is steadily increased by the anodic formation of
97 protons.

98
99 In a preferred embodiment of the process, the sulfuric acid of increased
00 concentration is carried out of the anolyte.

01
02 Additional advantageous embodiments of the process are given in claims 3 to
03 7.

04
05 An important advantage of the process is to be seen in the fact that the
06 sulfuric acid of increased concentration can be fed back into the etching or
07 extraction process as a fresh component of the solution, in a kind of recycling,
08 and that the cathodically precipitated metal can also be recycled.

09
10 The process can be operated either batch-wise or continuously. In batch
11 operation a solution is fed in as catholyte, in which the sulfuric acid
12 concentration is the same as the initial concentration in the anolyte. If,
13 however, the solution is continuously fed in as catholyte, its sulfuric acid



14 concentration must, as a rule, always be below the sulfuric acid concentration
15 of the anolyte. After a given thickness of the metal precipitate is reached, the
16 cathode is removed from the catholyte chamber. It is also possible, however,
17 to remove the precipitated metal from the cathode mechanically and remove
18 from the cell the granules thus obtained.

19
20 The purpose of the invention is attained as regards apparatus by the fact that
21 the ion exchanger membrane is configured as a cation exchanger membrane
22 and is stable against sulfuric acid, and that metal precipitated at the cathode
23 can be removed from the cell.

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25 Additional advantageous embodiments of the apparatus are specified in claims
26 9 to 14.

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28 The process according to the invention is used preferably as a follow-up
29 operation in an etching or extraction process in which, in a first step, a
30 solution containing chloride ions is converted by ion exchange methods to a
31 solution containing sulfate ions.

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33 An important advantage of the invention is to be seen in the fact that the metal
34 can be precipitated from a sulfate solution containing metal ions, in a simple,
35 cost-effective manner, while at the same time a continual increase is achieved
36 in the concentration of the sulfuric acid, which is recycled to continue the
37 regeneration process.

38
39 The subject matter of the invention is further explained hereinafter with the
40 aid of Figures 1 and 2.



Figure 1 shows schematically a longitudinal section through an electrolysis cell.

Figure 2 is a diagram of how the process operates in the form of a circuit.

The electrolysis apparatus has, in Figure 1, a tank 1 whose interior is divided by a cation exchanger membrane into a catholyte chamber 3 and an anolyte chamber 4. The anode 8 in the anolyte chamber 4 consists of a dimensionally stable valve metal electrode, especially a titanium electrode, which is connected to the positive pole 10 of a direct-current source 7. The principle of the design of such dimensionally stable valve metal electrodes, especially titanium electrodes, is known in chloralkali electrolysis, and described for example in DE-OS 20 41 250.

The cathode 5 in the catholyte chamber 3 consists of expanded copper metal; it is connected through a removable electrical terminal 9 to the negative pole of the direct-current voltage source 7. In the catholyte chamber 3 is an aqueous sulfuric acid solution, which when the process starts is fed through line 11 to produce the ion conduction, and water is added as needed during the electrolysis process, and the additionally forming sulfuric acid is removed through the outlet 12 of the catholyte chamber and fed back into the regeneration process, which is for example an etching procedure.

The sulfate solution containing zinc ions is fed, continuously for example, through line 15 to the anolyte chamber 4, wherein the sulfuric acid concentration in the anolyte amounts in practice to no more than that of the catholyte. The sulfuric acid concentration of the anolyte is in the neighborhood of 70 g/l. After the anolyte and catholyte chambers are filled the



electrolysis process begins: when the voltage source 7 is applied the charge moves during the electrolysis through the ion exchanger membrane 2 by means of the cations, which are indicated symbolically with reference number 13. The zinc ions are indicated symbolically by the reference number 14 and are discharged at the cathode 5, and metallic zinc is precipitated.

In the anolyte chamber the dissociation of water takes place, the oxygen being carried away as gas from the open-topped tank 1 and the hydrogen ions together with the sulfate ions are recombined to sulfuric acid, the concentration of which is raised in the course of the electrolysis process, and it exits through outlet 16 to the etching process. The sulfuric acid concentration of the catholyte is adjusted with the aid of pH meters and a control circuit which, by removing the more concentrated sulfuric acid and feeding in water through line 11, sustains the given sulfuric acid concentration or adapts it to the sulfuric acid concentration of the catholyte. The anolyte fed in as etching solution has a zinc ion concentration of about 170 g/l and a sulfuric acid concentration of around 70 g/l. The cathode 5 is made in the form of a copper-titanium or vanadium expanded metal mesh, while the anode 8 consists of the above-mentioned dimensionally stable titanium anode. Zinc is put onto the cathode 5 in a solid precipitate quality; it is also possible, however, to precipitate the zinc in dendritic form and then remove it from the cell tank. The current density of the cathode ranges from 50 to 2500 A/m².

The same electrolysis apparatus is used to advantage for a batch operation, wherein the catholyte is continuously removed within specific concentration ranges, while the anolyte side is replenished batch-wise.

According to Figure 2, the sulfate solution containing zinc ions and flowing



from the outlet 21 of an etching apparatus 20 is fed through line 15 to the anolyte chamber 4 of the one tank 1 that contains the electrolysis cell having the ion exchanger membrane, while the zinc precipitated in the catholyte chamber -- represented in the diagram by the reference number 22 -- is taken out of the catholyte chamber 3. The aqueous sulfuric acid solution of increased concentration forming in the anolyte chamber 4 is fed through outlet 16 and line 23 as fresh component for the etching process through inlet 24 of the etching apparatus 20.

Figure 2 shows how the solution containing sulfuric acid circulates according to the process; the used etching solution is fed as an aqueous sulfate solution containing metal ions through outlet 21 of the etching apparatus 20 and line 15 to the anolyte chamber 4 of the cell, while the virtually pure sulfuric acid of increased concentration is fed back through line 23 to the etching process.

The precipitated zinc is collected from this continuously circulating process by removing it from the cell, and it can also be recycled. A membrane of the type named NAFION supplied by Dupont is used as the cation exchanger membrane.

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Claims

1. Process for the regeneration of an aqueous solution containing metal ions and sulfuric acid, especially a solution containing zinc ions, nickel ions, iron ions and/or copper ions, in an electrolytic cell, wherein the metal ions are precipitated on the surface of the cathode and oxygen and protons are formed at the anode by the dissociation of water, and regenerated solution can be recycled to a preceding etching process or extraction process, characterized in that the metal ion-containing solution, as the anolyte with a sulfuric acid concentration of about 60 to 80 g/l, is fed into an electrolysis cell divided by the use of a cation exchanger membrane stable against sulfuric acid, and that the cathodic precipitation is performed at a current density in the range from 50 to 2500 A/m², wherein cations migrate from the anolyte through the cation exchanger membrane, on the basis of the voltage applied to the electrodes, and are discharged, the sulfuric acid concentration in the anolyte being constantly increased by anodic formation of protons.
2. Process according to claim 1, characterized in that the sulfuric acid of increased concentration is removed from the anolyte.
3. Process according to claim 1 or 2, characterized in that a solution whose sulfuric acid concentration corresponds in each case to the initial concentration of the catholyte is fed as anolyte batchwise to the electrolysis cell.
4. Process according to claim 1 or 2, characterized in that a solution whose sulfuric acid concentration is always below the sulfuric acid concentration





of the catholyte is fed continuously as anolyte to the electrolysis cell.

5. Process according to any one of claims 1 to 4, characterized in that after a given amount is reached, the cathodic metal precipitate is removed from the cell.
6. Process according to claim 5, characterized in that the cathode is removed from the cell after reaching a given thickness of the layer of the metal precipitate.
7. Process according to claim 5, characterized in that the metal precipitate is removed from the cell after separation from the cathode.
8. Apparatus for the regeneration of an aqueous solution containing metal ions and sulfuric acid in an electrolysis cell having at least one anode and one cathode, the electrolysis cell being divided by an ion exchanger membrane into an anolyte chamber and a catholyte chamber, and the catholyte chamber has at least one opening for the introduction and removal of the solution containing metal ions, and the anolyte chamber has at least one opening for the introduction and removal of the regenerated solution, characterized in that the ion exchanger membrane (2) is configured as a cation exchanger membrane and is stable against sulfuric acid, and that metal precipitated at the cathode (5) is removable from the cell.
9. Apparatus according to claim 8, characterized in that the cathode (5) is electrically and mechanically releasable for the removal of the precipitated metal.



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- 73 10. Apparatus according to claim 9, characterized in that a separation and
74 transport system is provided for separating the precipitated metal from the
75 cathode (5) and bringing it out of the catholyte chamber.
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- 77 11. Apparatus according to claim 8, characterized in that the anode (8)
78 consists substantially of valve metal.
79
- 80 12. Apparatus according to claim 8 or 11, characterized in that the anode (8)
81 is a dimensionally stable electrode on the basis of titanium.
82
- 83 13. Apparatus according to any one of claims 8 to 12, characterized in that
84 the anolyte chamber (4) has an opening for the input of water or of an
85 aqueous solution.
86
- 87 14. Apparatus according to any one of claims 8 to 13, characterized in that
88 the catholyte chamber (3) has an opening for the input of water or of an
89 aqueous solution.

